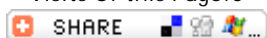




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Research Details :

Research Title	: <u><i>Kinetic Solvent Effects for Nucleophilic Attack on Ester Linkage</i></u> <u>تأثيرات المذيب الحركية في الهجوم النيوكليوي فيلي على الارتباط الإستري</u>
Descriptipn	: The reaction of 4-nitrophenylacetate in aqueous and ethanol solutions with imidazole as a nucleophile was monitored spectrophotometrically by following the appearance of the generated 4-nitrophenyloxide ion, under pseudo-first order conditions and at four temperature viz 5,10,15 and 20°C. The second order nature of the reaction was established from the linear dependance of the pseudo first order rate constant kobs with the imidazole concentration: The second order rate constants was 10 times higher in water than in alcohol solutions. This was attributed to better solvation of the initial state and less solvation of the excited state in the alcohol medium resulting into a higher energy barrier for the reaction in alcohol and a smaller rate constant value. The entropy of activation in water was more negative indicating the greater structured ness of the excited state in water, because of the greater hydrogen bonding. Inthese systems the solvolysis rates were negligible in comparison to the nucleophilic attack and the intercept of the line ofkobs vs. imidazole concentration was zero within experimental error. In addition to the above the base hydrolysis reaction of the ester using HO. as a nucleophile in buffered aqueous solutions was followed spectrophotometrically as a function of pH. The observed pseudo first order rate constant obeyed the relationship $k_{obs}=k_o+k_{oH} [-OR]$ where k_o represents the water reactions and the buffer dependent rate constant, where as k_{oH} is the rate constant for the HO- catalyzed (specific base) reaction. In all cases a mechanism involving a tetrahedral intermediate, in which the nucleophile attacks at the electrophilic carbon of the ester C=O, breaking the 7t bond and forming the tetrahedral intermediate. The intermediate, however, has no significant lifetime and hence a concerted bond-formation and bond-breakage proposed for the reaction.
Research Type	: Master
Supervisor	: د/ سالم بن أحمد باسيف و أ.د/ عباس بن عباس العوضي
Added Date	: Thursday, June 12, 2008

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